The Atomic Weight
of
Palladium

THESIS

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THE ATOMIC WEIGHT OF PALLADIUM.

The atomic weight of palladium has been the subject of no less than twelve separate investigations. The results vary so widely that it seemed advisable to give it still further consideration.

The previous work is most easily summed up by means of the following table:

Date.	Author.		Salt used.	Determined.	O = 6	H = 1.
1826	Berzelius	1	Pd	PdS	114.3	
1828	Berzelius	2	K_2PdCl_4	Pd-Cl_2-KCl	106.5	
1847	Quintus Icilius	3	K_2PdCl_4	Pd.		111.8
1889	Keiser	4	$Pd(NH_3Cl)_2$	Pd	106.54	106.31
1892	Bailey and Lamb	5	$Pd(NH_3Cl)_2$	Pd and Cl_2	105.731	105.45
1892	Keller and Smith	6	$Pd(NH_3Cl)_2$	Pd	107.19	106.91
1893	Joly and Leidie	7	K_2PdCl_4		105.71	105.92
1894	Keiser and Breed	8	$Pd(NH_3Cl)_2$	Pd	106.518	106.25
1899	Hardin	9	$(NH_4)_2PdBr_4$	Pd		
			$Pd(C_6H_5NH_2Cl)_2$	Pd	107.01	106.74
			$Pd(C_6H_5NH_2Br)_2$			
1906	Krell	10	$Pd(NH_3Cl)_2$	Pd	106.69	
1906	Amberg	11	$Pd(NH_3Cl)_2$	Pd	106.7	
1907	Woernle	12	$Pd(NH_3Cl)_2$	Pd	106.71	

1. Berzelius. Pogg Ann. 8, 180, 1826.
2. " Pogg Ann. 13, 454, 1828.
3. Quintus Icillius. Clark. Atomic Weights, 315.
4. Keiser. Amer. Chem. J. 11, 398. 1889.
5. Bailey and Lamb, J. Chem. Soc. 61, 745, 1892.
6. Keller and Smith, Amer. Chem. J. 14, 423, 1892.
7. Joly and Leide, Compt. Rend. 116, 146, 1893.
8. Keiser and Breed, Amer. Chem. J. 16, 20, 1894.
9. Hardin. J. Am. Chem. Soc. 21, 943, 1889.
10. Krell, Dissertation, Erlangen, 1906.
11. Amberg, Lieb. Ann. 341, 235, 1905.
12. Woernle Dissertation, Erlangen, 1907.

Purification of Materials.

The metal was obtained from Baker and Adamson as sheet palladium and weighed 32 grams. Sample No. 1 was purified according to the method of Keller and Smith[1] and was used to prepare salt (A). Sample No. 2 was treated similarly, but the use of mercuric cyanide was eliminated and sodium and potassium salts were replaced by similar ammonium compounds wherever possible.

The complete process was as follows. The metal was dissolved in aqua regia and repeatedly evaporated with hydrochloric acid to remove the nitric acid. The residue was then

(1) Keller and Smith, Amer. Chem. J. 14-423, 1892.

taken up in a little dilute hydrochloric acid and filtered. The concentrated solution of palladous chloride was treated with an excess of ammonia and warmed. The palladium dissolved leaving a brownish residue of ferric hydroxide and an insoluble rhodium compound. These were filtered out, the solution heated to expel the excess of ammonia and when cool, hydrochloric acid was added until just acid. The pallado-diammonium chloride separated in small bright yellow crystals. These were washed by decantation, filtered on a suction filter, washed with cold water and dissolved in a little cold dilute ammonia. A trace of an insoluble rhodium compound remained on the filter. The filtrate was now heated to expel the excess of ammonia and the pallado-diammonium chloride reprecipitated by acidifying with hydrochloric acid. This precipitate was washed, dried and carefully ignited in the air to the green oxide. The oxide was then placed in a rose crucible and reduced in hydrogen to the metal, which was dissolved in aqua regia and repeatedly evaporated with hydrochloric acid. The chloride remaining was taken up in a little dilute hydrochloric acid, diluted to two liters and nearly neutralized with sodium carbonate. The solution was then treated with an equivalent quantity of ammonium cyanide and the resulting yellow palladium cyanide was washed by decantation for one week. It was filtered by means of an invert filter and dried. The dry cyanide was placed in an unglazed porcelain crucible, contained in a similar larger crucible. Each crucible was covered and the whole heated at the highest temperature of the muffle furnace for six hours. The resulting metal was treated with concentrated hydrochloric acid to remove any oxide of copper and again dissolved in aqua regia. The nitric acid was removed by evaporation with hydrochloric acid and the chloride dissolved with a little dilute hydrochloric acid and diluted to two liters. This solution was saturated with sulphur dioxide, treated with ammonium sulpho-cyanide and allowed to stand for two days, but no precipitate was formed. The sulphur dioxide was now expelled by heating on the waterbath when the solution returned to its original color and a little palladium was precipitated. This was filtered out, the solution treated with ammonium formate and nearly neutralized with ammonia. On heating the solution the metal was almost completely precipitated. The black palladium, filtered out and thoroughly washed, was dried and heated in a double crucible, similar to the one used for the cyanide, to the high-

est heat of the muffle for six hours. When cool, the slight tarnish of oxide was removed by treating with hydrochloric acid, after which the metal was silver white in color.

Water. The water for the preparation of salt A was only distilled once. For all the other work it was redistilled from glass using a block tin condenser and Jena glass receiving flasks.

Hydrochloric Acid. Hydrochloric acid was diluted and distilled from an apparatus constructed entirely of glass. The first and last portions of the distillate were rejected, only the middle portion being used.

Sodium Carbonate. So-called pure carbonate of soda was recrystallized once from porcelain and three times from platinum, drying each time centrifugally.

Mercuric Cyanide. Mercuric oxide was first prepared by treating a solution of sublimed mercuric chloride with sodium hydroxide made from sodium. This was thoroughly washed and dissolved in hydrocyanic acid, made by distilling the freshly prepared anhydrous acid into water. The solution was then evaporated, and allowed to crystallize. The salt was recrystallized from water and dried centrifugally.

Ammonium Formate. Formic acid was distilled, diluted and neutralized with ammonia gas. The solution was then evaporated when ammonium formate crystallized out.

Sulphur dioxide. Dioxide of Sulphur was made by treating a solution of sodium acid sulphite with concentrated sulphuric acid. The gas was washed with water and sulphuric acid.

Ammonium Sulpho cyanate. Sulpho cyanate of ammonium was crystallized from alcohol, then recrystallized from water.

Preparation of Salts. Salt A, pallado-diammonium chloride, was prepared from the sample of pure metal No. I. It was dissolved in aqua regia and evaporated to dryness five times with hydrochloric acid. The chloride was finally taken up with as little dilute hydrochloric acid as possible, the solution filtered through a hardened filter and treated with an excess of ammonia gas. When this was warmed the red pallado-ammonium salt went completely into solution. An excess of hydrochloric acid was then added to the ammoniacal solution,

when the pallado-ammonium chloride separated in small yellow crystals. These were filtered out on a hardened filter and washed with cold water. After being removed from the moist filter they were dried over sulphuric acid, then powdered and brought to constant weight by heating at 110°C.

Salt B. The pallado-diammonium chloride lettered B was prepared similarly to A except that the metal used was part of sample No. 2.

Salt C. The pallado-diammonium cyanide $Pd(NH_3CN)_2$ was prepared from metal No. 2. The metal was dissolved in aqua regia, freed from nitric acid and the chloride dissolved in dilute hydrochloric acid. This solution was then diluted and treated with an equivalent quantity of ammonium cyanide containing a slight excess of ammonia. By this method the cyanide was precipitated almost completely without neutralizing the hydrochloric acid with sodium carbonate. The yellow gelatinous cyanide was washed by decantation for two weeks which completely freed it from chlorine. The water was then removed as completely as possible and ammonia gas conducted into the suspended cyanide. It dissolved readily and completely. The excess of ammonia was expelled by warming on the water bath and on cooling the pallado-diammonium cyanide crystallized in small, beautiful white crystals. These were separated on a hardened filter, and thoroughly washed with water. They were then dried over phosphorus pentoxide and powdered. The salt was brought to constant weight by heating to 45°C in a vacuum desiccator over phosphorus pentoxide. A trial sample of the salt was treated in a desiccator heated by a small incandescent lamp. Constant weight was obtained after two weeks' heating, but the salt darkened very slightly on the surface. In order to overcome this difficulty the desiccator was coated with black varnish and heated by a coil of resistant wire carrying a current of 0.4 of an ampere. This gave a temperature varying from 43 to 46° and the salt was constant in weight after two weeks' heating.

Weighing.

All weighings were made on a Troemner balance which has been used exclusively for atomic weight work in this laboratory. It was sensitive to .02 of a milligram and duplicate weighings of the same thing seldom varied more than .03 of a milligram. The brass and platinum weights were carefully calibrated and checked during the year. The salt to be re-

duced was weighed in a porcelain boat contained in a weighing bottle. These were counterbalanced by a similar tube and boat of equal weight. All weights were reduced to the vacuum standard using the following specific gravities: Palladium metal, 11.45; pallado-diammonium chloride, 2.55; pallado-diammonium cyanide, 2.5. During the course of the experiments the glaze on the boat gradually darkened, probably due to the absorption of minute traces of palladium. Platinum boats were tried, but it was not possible to heat them sufficiently high without danger of alloying. To eliminate any possible error from the absorption of palladium, after each experiment the boat was boiled in aqua regia and soaked in hot water. It was then dried and heated to bright redness in hydrogen for one hour. After cooling in nitrogen it was removed to the desiccator and allowed to stand in the balance room for two hours before weighing. While using this method the weight of the boats did not vary more than .03 of a milligram between any two consecutive experiments.

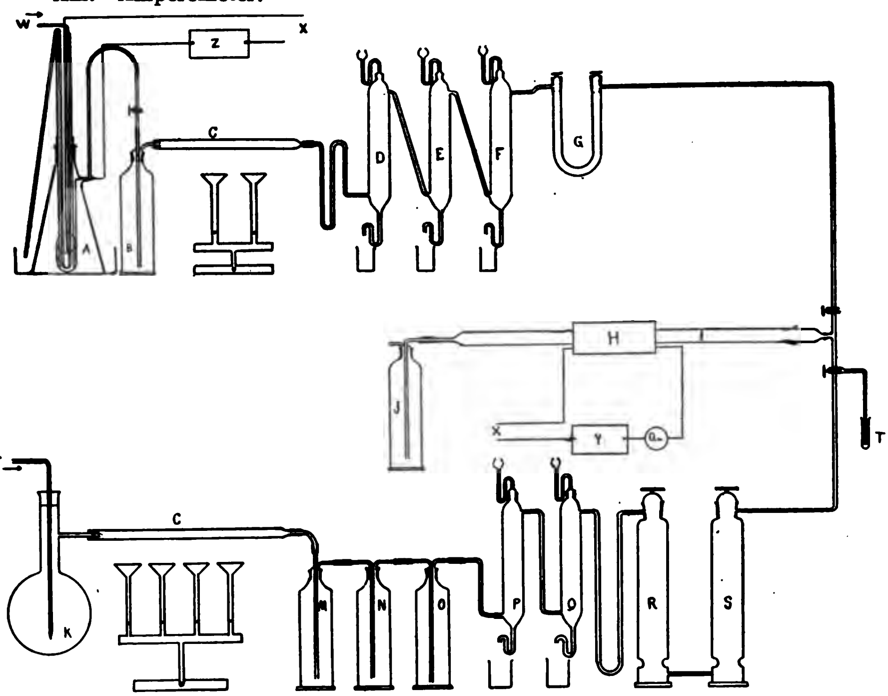
The Reduction Apparatus.

The reduction of the salt to metal was carried out in an apparatus which is most easily understood by means of the accompanying sketch. Electrolytic hydrogen was prepared by passing a current of six amperes through a solution of sodium hydroxide. The platinum electrodes were so arranged that no oxygen could diffuse into the hydrogen compartment and the electrolyte was cooled by passing water through a coil of glass tubing immersed in the anode compartment. The hydrogen thus generated passed through a wash bottle containing concentrated sulphuric acid, then over red hot copper to remove any oxygen or hydrogen peroxide which might be present. The gas next passed through an apparatus made entirely of glass composed of towers containing glass balls. In the first tower the balls were moistened with a solution of silver nitrate. The second and third contained concentrated sulphuric acid. The drying was then completed in a U tube containing phosphorus pentoxide, from which the hydrogen passed directly to the combustion tube.

The nitrogen was prepared by passing ammonia gas and air over red hot copper. The excess of ammonia was absorbed by passing the gas through three wash bottles containing dilute sulphuric acid. The nitrogen was purified by passing

Explanation of Cut.

A. Hpdrogen generator.
B. Sulphoric acid wash botttle
C. Combination tubes containing copper gauze.
D. Silver nitric tower.
E. and F. Sulphuric acid towers.
G. U. tube containing phosphorus pentoxide.
H. Electric Heating coil.
I. Combination tube.
J. Sulphuric Acid trap.
K. Ammonia flask.
L. Air supply.
M. N. O. Wash bottles containing dilute sulphuric acid,
P. Silver nitrate tower.
Q. Tower containing concentrated sulphuric acid.
R. Fused potassium hydroxide tower.
S. Tower containing phosphorus pentoxide.
T. Trap for escape of nitrogen.
W. Water for cooling coil.
X. 100 volt direct current.
Y. Lamp bank resistance.
Z. Resistance box.
Am. Amperemeter.



it through a series of towers constructed entirely of glass containing the following re-agents in the order mentioned: a solution of silver nitrate, concentrated sulphuric acid, fused potassium hydroxide, and phosphorus pentoxide. From the last tower the gas passed to the two-way stopcock by means of which it was admitted to the combustion tube or allowed to escape into the air through a sulphuric acid trap. This trap was necessary in order to entirely free the apparatus of air while the hydrogen was passing through the combustion tube.

The Jena tube in which the reduction took place was connected with the apparatus by a carefully ground joint which was not lubricated, but held in close contact by a rubber band. The farther end of the tube was supplied with a sulphuric acid trap to prevent the entrance of air.

This tube was heated with an electric heater made by covering a sheet iron tube with asbestos then winding it with 6 feet of No. 32 platinum wire. The whole was covered with several thicknesses of asbestos to prevent loss of heat. The current supplied the heater was controlled by a lamp bank resistance and varied from 0.25 to 1.6 of an ampere. By this means the temperature could be raised very gradually until the salt was reduced and the ammonium compound volatilized.

Reduction of the Pallado-Diammonium Compounds.

The counter-balanced boat was filled with salt and after standing in the balance room for two hours it was weighed. The boat and its contents were then transferred to the combustion tube where the boat rested on a piece of platinum foil. The apparatus was then closed, the hydrogen generator started and 0.25 ampere allowed to flow through the heating coil for two hours. The current was then raised to 0.5 ampere which completed the reduction in another hour. The current was now gradually increased to 1.6 amperes which heated the boat and contents to 955°.* With the pallado-diammonium chloride the metal usually came to constant weight after heating for five hours. The hydrogen and heating currents were then broken and nitrogen passed through the tube while it cooled, which required about one hour. The boat was then placed in its weighing bottle and weighed after it attained the temperature of the balance room. This weight was checked by heating in hydrogen for two

*This temperature was determined by melting finely divided silver in a boat placed within the tube.

hours and cooling in nitrogen as before. No weight was accepted which did not check to 0.05 milligram or less.

The reduction of the double cyanide was similar, only it required 8 to 10 hours heating in hydrogen to bring it to constant weight.

By this method the reduction and volatilization of the ammonium salts took place very slowly so that there was very little chance of any palladium being carried out of the boat by the volatile salts; but in order to be sure of this, the combustion tube was washed out with aqua regia and water after each experiment, and the solution carefully tested for palladium, but always with negative results.

The following results were obtained by the reduction of salts in hydrogen, using the following values: Chlorine 35.473, hydrogen 1.008, nitrogen 14.01.

Pallado-diammonium chloride. $Pd(NH_3Cl)_2$. A.

	Weight of Salt.	Weight of Metal	Atomic Weights. O = 16
1.	0.89187	0.44885	106.40
2.	0.77931	0.39218	106.38
3.	0.66980	0.33711	106.41
4.	1.08373	0.54541	106.40
5.	0.96048	0.48338	106.40
		Mean, —	106.399

Pallado-diammonium chloride. $Pd(NH_3Cl)_2$. B.

1.	0.95615	0.48129	106.43
2.	0.94087	0.47356	106.42
3.	0.90106	0.45353	106.42
4.	1.16994	0.58908	106.50
		Mean, —	106.442

Pallado-diammonium cyanide. $Pd(NH_3CN)_2$. C.

1.	0.85860	0.47463	106.41
2.	1.19378	0.66002	106.45
3.	1.41818	0.78408	106.45
4.	1.05254	0.58206	106.51
5.	1.39510	0.77153	106.51
6.	1.66196	0.91881	106.42
		Mean, —	106.458
		The mean of the 15 determinations,	106.434

The Electro-chemical Equivalent of Palladium.

When this work was started we hoped to be able to determine the electro-chemical equivalent of palladium as compared to silver. Numerous experiments were tried using the

Richards type coulometer, but the results were never concordant. About this time L. Wöhler and F. Martin[1] stated that palladium used as the anode in nitric acid solution was oxidized to Pd_2O_3 and PdO_2. This explained our variable results and seems to prove the method useless for atomic weight work.

Pallado-Diammonium Chloride.

When this salt is prepared as described there are often a few dark red crystals which form with the ordinary light yellow variety. This seems to be only a dimorphous form, for the red crystals are not soluble in water and they disappear on drying, but palladium ammonium chloride $(NH_4)_2PdCl_4$ is formed by the addition of ammonium chloride to a solution of palladous chloride. A trace of it might be formed along with the pallado-diammonium chloride, since the excess of ammonia is neutralized with hydrochloric acid. Such does not seem to be the case for if the double chloride were present it would tend to lower the per cent. of palladium. To determine this point a sample of the diammonium chloride was washed with very dilute hydrochloric acid for one week then washed with water for one day. After drying to constant weight the per cent. of palladium was slightly higher than from the unwashed samples.

1 Wöhler and Martin, Chem. Zeit. March 25, 1908.

Conclusions.

The results of these fifteen determinations give a mean of 106.434, which is slightly lower than most previous determinations. The metal was very carefully purified so that it seems improbable that the difference could be accounted for here. In the reductions the metal was heated to a much higher temperature, 955°C, than by previous investigators. This may have expelled the ammonium chloride more completely, but it does not seem sufficient to account for the difference. Variations in th pallado-diammonium chloride seem to be a possible source of difference.

It is hoped that the work may be continued, determining the constancy of pallado-diammonium chloride, using metal from different sources and determining new ratios, if possible.